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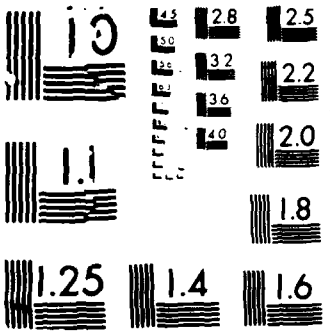
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DSC, Electrical Conductivity, and NMR Studies of Salt Precipitation Effects in PPO Complexes

by

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DSC and electrical conductivity measurements of PPO complexed with NaI and KSCN are reported. In additional, ^{23}Na NMR measurements of PPO$_8$NaI, both at ambient and elevated pressure (2.0 kbar) have been performed. The DSC data clearly indicate that the salt precipitates out of the complexes at about 85°C for NaI and 60°C for KSCN. These effects are manifested by a dramatic departure of the conductivity from VTF behaviour, and a relatively sharp drop in mobile Na concentration deduced from NMR measurements at somewhat elevated temperature ($\sim$ 80°C). High pressure NMR linewidth measurements are consistent with a pressure-induced increase in glass transition temperature.

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DSC, Electrical Conductivity, and NMR Studies of Salt Precipitation Effects in PPO Complexes

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Keywords: ion-conducting polymer; salt precipitation; NMR; DSC; poly(propylene oxide)

SYNOPSIS

DSC and electrical conductivity measurements of PPO complexed with NaI and KSCN are reported. In addition, ^{23}Na NMR measurements of PPO_8NaI, both at ambient and elevated pressure (2.0 kbar) have been performed. The DSC data clearly indicate that the salt precipitates out of the complexes at about 85°C for NaI and 60°C for KSCN. These effects are manifested by a dramatic departure of the conductivity from VTF behaviour, and a relatively sharp drop in mobile Na concentration deduced from NMR measurements at somewhat elevated temperature (~ 80°C). High pressure NMR linewidth measurements are consistent with a pressure-induced increase in glass transition temperature.

INTRODUCTION

Poly(propylene oxide) (PPO) is known to form amorphous ion conducting complexes with alkali metal salts.[1-3] Previous studies of PPO complexed with $LiClO_4$[2] and $NaClO_4$[3] have shown that large scale segmental motion of the polymer chains is principally responsible for ionic transport, in general agreement with the results of a wide array of recent investigations. The studies in our laboratories[2,3] can be summarized briefly as follows. The electrical conductivity temperature dependence is best described by a VTF-type relation[4]

$$\sigma = A\, T^{-1/2} \exp[-E_a/k(T - T_o)] \qquad (1)$$

where E_a is the apparent activation energy and T_o is the temperature of "zero configurational entropy", about 40-50 K below the glass transition temperature, T_g. The temperature dependence of the electrical relaxation time associated with the -relaxation which governs the glass to rubber transition in pure PPO can be described in an analogous manner. It has been shown that the activation energies for conductivity in the complexes and electrical relaxation in pure PPO are the same when one takes into account the different T_o values associated with each material. Similarly, activation volumes for conductivity derived from variable pressure data in the complexes and the -relaxation in PPO were shown to be the same in a given temperature interval relative to T_o.

^{23}Na NMR studies in PPO_8NaClO_4 have shown that: (1) generation of mobile ions is a weakly thermally activated process that accounts for only a minor contribution to the overall conductivity; (2) NMR signals associated with the mobile fraction of Na ions exhibit motional line-narrowing beginning in a small temperature interval above T_g. These results, taken together, demonstrate the importance of polymer chain mobility to ion transport, in general agreement with a wide array of recent investigations.

The present study concerns related work on PPO:NaI and PPO:KSCN complexes. In particular, it is observed that these materials

exhibit behaviour similar to that of previously investigated PPO complexes, however they become unstable at moderate temperatures (<100°C). As will be discussed, the instability is manifested ultimately by the separation of the salt from the polymer.

We have performed differential scanning calorimetry (DSC), electrical conductivity and ^{23}Na nuclear magnetic resonance (NMR) measurements on PPO_8NaI. The NMR measurements were performed both at ambient pressure and at applied hydrostatic pressure up to 2 kbar (0.2 GPa). In addition, DSC and conductivity data for PPO_8KSCN are presented.

EXPERIMENTAL

The host material studied was Parel 58 (Hercules, Inc.) elastomer which is a sulfur-vulcanizable copolymer of propylene oxide and allyl glycidyl ether. As the primary constituent is propylene oxide, the material will be referred to throughout this paper as PPO. The samples were prepared by solution casting using anhydrous methanol as the solvent and commercially obtained NaI, which was heated at 100C in a vacuum oven overnight, as the salt. All procedures including loading of the samples into the various sample holders were carried out in a dry box; the sample for the NMR measurements was sealed in a glass tube under dry nitrogen. For the high pressure measurements, the sample was loaded into the rf coil in a N_2 glove bag and then immersed in the pressure transmitting fluid (3M - Fluorinert) contained in the pressure cell. The details regarding the DSC, electrical conductivity and NMR equipment and techniques are given elsewhere.[2,3]

RESULTS

The DSC results for PPO_8NaI are shown in Fig. 1. Results for uncomplexed PPO are included for comparison. It is clear that the complexed material is highly amorphous in that it exhibits a strong glass transition with a "central" T_g of about 6°C. (The "onset" T_g is about 0°C and the "end" is at about 12°C.) Consequently, T_g is about 68°C higher than for the uncomplexed material for which the

"central" glass transition temperature is about -62°C as shown in Fig. 1c. An increase in T_g with the addition of salt to PPO is a well known phenomenon[2].

In addition, in the DSC studies for PPO_8NaI, a strong, sharp endothermic event is observed at about 100°C. In order to obtain information concerning this feature, the material was annealed at 175°C, quenched to -140°C as rapidly as possible in situ, and the DSC studies repeated. Typical results for the quenched material after annealing at temperatures above 140°C are shown in Fig. 1b. In all cases, a strong glass transition typical of uncomplexed PPO is observed. In addition, there is a high temperature exothermic event followed by an endotherm. Similar behavior has been observed for PPO_8NaClO_4 where it was concluded that the high temperature endotherm is due to the salt coming out of the polymer.[3] The primary evidence is that only the glass transition due to uncomplexed PPO is observed after quenching from temperatures above that of the sharp endotherm. Further, the material exhibits the original behavior (Fig. 1a) after allowing the sample to sit at room temperature overnight, i.e. the salt redissolves in the polymer. Salt precipitation has been observed spectroscopically for PPO containing NaSCN.[5]

In order to gain further evidence for this effect, electrical conductivity studies were performed. (It was not possible to perform such studies for PPO_8NaClO_4 as the salt precipitation temperature was outside the range of the conductivity apparatus.) The results are shown in Fig. 2. It is seen that the electrical conductivity begins to deviate from its lower temperature behavior at about 85°C. In order demonstrate this more quantitatively, the data in the temperature range 280-355 K were analyzed with equation (1) with the adjustable parameters A, E_a, and T_o. A non-linear least squares fit of eq. (1) to the data was carried out and the results are E_a = 0.093 eV, T_o = 199.3 K, and $\log_{10}A$ [$(\Omega\text{-cm})^{-1}$ $K^{1/2}$] = -1.1. The RMS deviation in $\log_{10}\sigma$ was 0.008. These best-fit values are close to these observed for other salts in PPO. However, they are not as reliable due to the limited temperature range covered, and further, the high temperature cut-off (where salt precipitation becomes

important) is merely an estimate. In fact, the value for T_o is about 80 K lower than the "central" T_g, which is a larger difference than expected.

A general feature of the ^{23}Na NMR results is the coexistence of two separate lineshape components with substantially different spin-lattice relaxation times (T_1) and linewidths. As in previous studies of similar complexes, the long-T_1 and broad component is attributed to bound Na species while the short-T_1 and narrow component arises from mobile Na^+ ions.[3] The ratio of the narrow line to broad line intensities as a function of reciprocal temperature is plotted in Fig. 3. That the difference between the lowest temperature value and the maximum value (occurring just above room temperature) is only about a factor of ten is indicative of the relatively minor role that "carrier generation" plays in the overall conductivity, which changes by more than four orders of magnitude over the same temperature range. The salt precipitation is manifested as a sharp drop in mobile ion concentration above 80°C.

Figure 4 is a plot of ^{23}Na resonance linewidth (full width at half maximum) as a function of temperature. The open symbols denote partially saturated resonances which correspond to the mobile sodium population. The solid symbols refer to the total (unsaturated) linewidth. As in previous work[3], the linewidths of the mobile and bound Na's are nearly indistinguishable below T_g, only their T_1 values are distinct. It is clear from the data that motional narrowing occurs above T_g, again in agreement with previous studies. The increase in linewidth above ~ 60°C is attributable to rapid spin-lattice relaxation (T_1 ~ 300 μs) which introduces a lifetime broadening contributions to the linewidth.

The application of hydrostatic pressure (up to several kbar) has been shown to result in a decrease in conductivity of PPO complexes[2,3]. In order to obtain a better understanding of the mechanisms involved, we have performed some preliminary high pressure NMR measurements. Figure 5 displays ^{23}Na absorption spectra (both lineshape components are present in each spectrum) at - 40°C, where motional narrowing effects are apparent. The bottom

spectrum corresponds to ambient pressure, while the top spectrum was acquired at 2.0 kbar (0.2 GPa). The effect of the applied pressure is to broaden the resonance by about 25% to approximately the linewidth of the sample at lower temperatures (below T_g). This result is consistent with increases in T_o with pressure deduced from conductivity measurements[2,3]. It is not presently known whether these phenomena simply reflect the pressure dependence of T_g, or are indicative of more subtle ion-polymer interactions. High pressure DSC measurements are currently underway in order to determine directly the T_g pressure-dependence. Conductivity vs. pressure studies, which may shed light on the salt precipitation process, are also in progress.

Another example of this salt precipitation is evident upon viewing the data for PPO_8KSCN, shown in Figs. 6 and 7. For this material, the salt comes out of the polymer at a lower temperature, about 60°C as seen by a sharp endotherm at about 60°C in Fig. 6. That the material was complexed is shown by the single glass transition temperature at about -25°C. Once again, upon thermal treatment, the glass transition disappears with the appearance of an uncomplexed PPO glass transition. This material is interesting because the melting endotherms for the salt are at relatively low temperature as shown in Fig. 6a. As shown in Figs. 6b and 6c, similar endotherms are observed in the polymer after heating above 60°C. Since the salt precipitation occurs at a relatively low temperature, the effect on the electrical conductivity is quite dramatic as shown in Fig. 7.

CONCLUSIONS

PPO complexed with NaI has been shown to exhibit the same general ion-conducting properties as other PPO-salt complexes at lower temperatures, whereas salt precipitation effects are observed in the former above ~ 85°C. The salt precipitation is manifested by (i) a relatively sharp endothermic "event" in the DSC, and subsequent observation of a pure PPO glass transition (after quenching); (ii) departure of the electrical conductivity from VTF-type behavior at elevated temperatures; (iii) a sharp drop in mobile

Na concentration, deduced from NMR measurements, above ~ 80°C. PPO complexed with KSCN exhibits even more dramatic salt precipitation effects, as evidenced by corresponding features in the DSC and conductivity data occuring at a lower temperature (~ 60°C) as well as observation of KSCN melting endotherms in the complex. Preliminary NMR measurements on PPO_8NaI at an applied hydrostatic pressure of 2.0 kbar (0.2 GPa) are consistent with a pressure-induced increase in T_g.

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FIGURE CAPTIONS

Figure 1. DSC plot for a) uncomplexed PPO, b) as prepared PPO_8NaI, and c) PPO_8NaI after having been annealed at 175°C and quenched, in situ, to -140°C. Scanning rate is 10 K/min.

Figure 2. Arrhenius plot of the electrical conductivity data for PPO_8NaI. The squares correspond to the data and the solid line is the best fit VTF equation (equation 1).

Figure 3. Arrhenius plot of ^{23}Na narrow to broad line intensity ratios in PPO_8NaI.

Figure 4. ^{23}Na linewidth in PPO_8NaI. The solid symbols denote the total linewidth while the open symbols refer to partially saturated resonances, reflecting the presence of only the mobile sodium population.

Figure 5. ^{23}Na absorption spectrum in PPO_8NaI at 40°C. Bottom: ambient pressure; Top: applied hydrostatic pressure of 2 kbar (0.2 GP_a).

Figure 6. DSC plot for a) KSCN, b) PPO_8KSCN, c) PPO_8KSCN after having been annealed at 200°C and quenched, in situ, to -140°C, d) uncomplexed PPO. Scanning rate is 10 K/min.

Figure 7. Arrhenius plot of the electrical conductivity data for PPO_8KSCN. The solid line connects the data points.

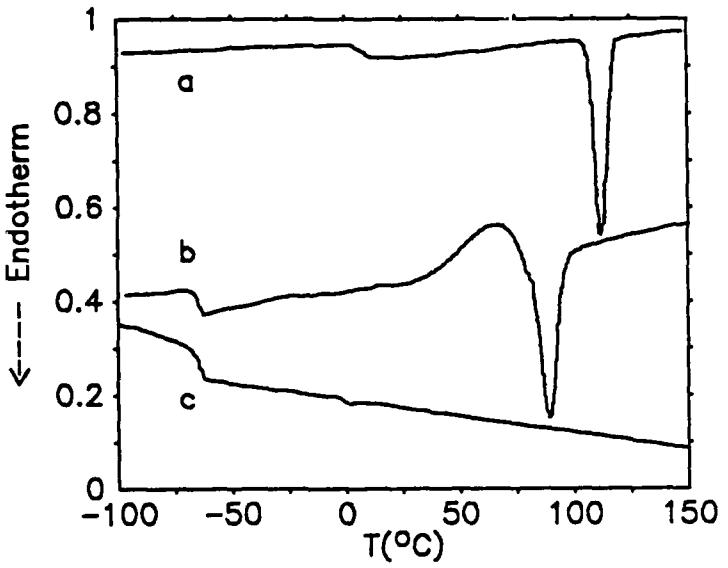
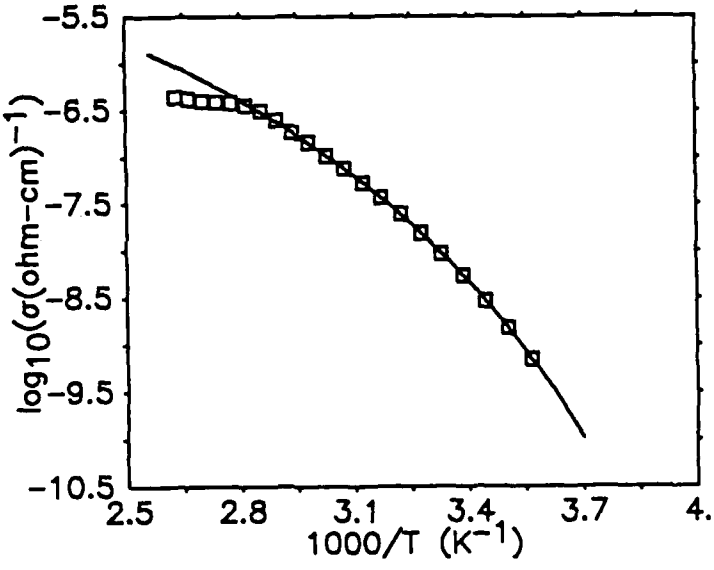


Fig. 1



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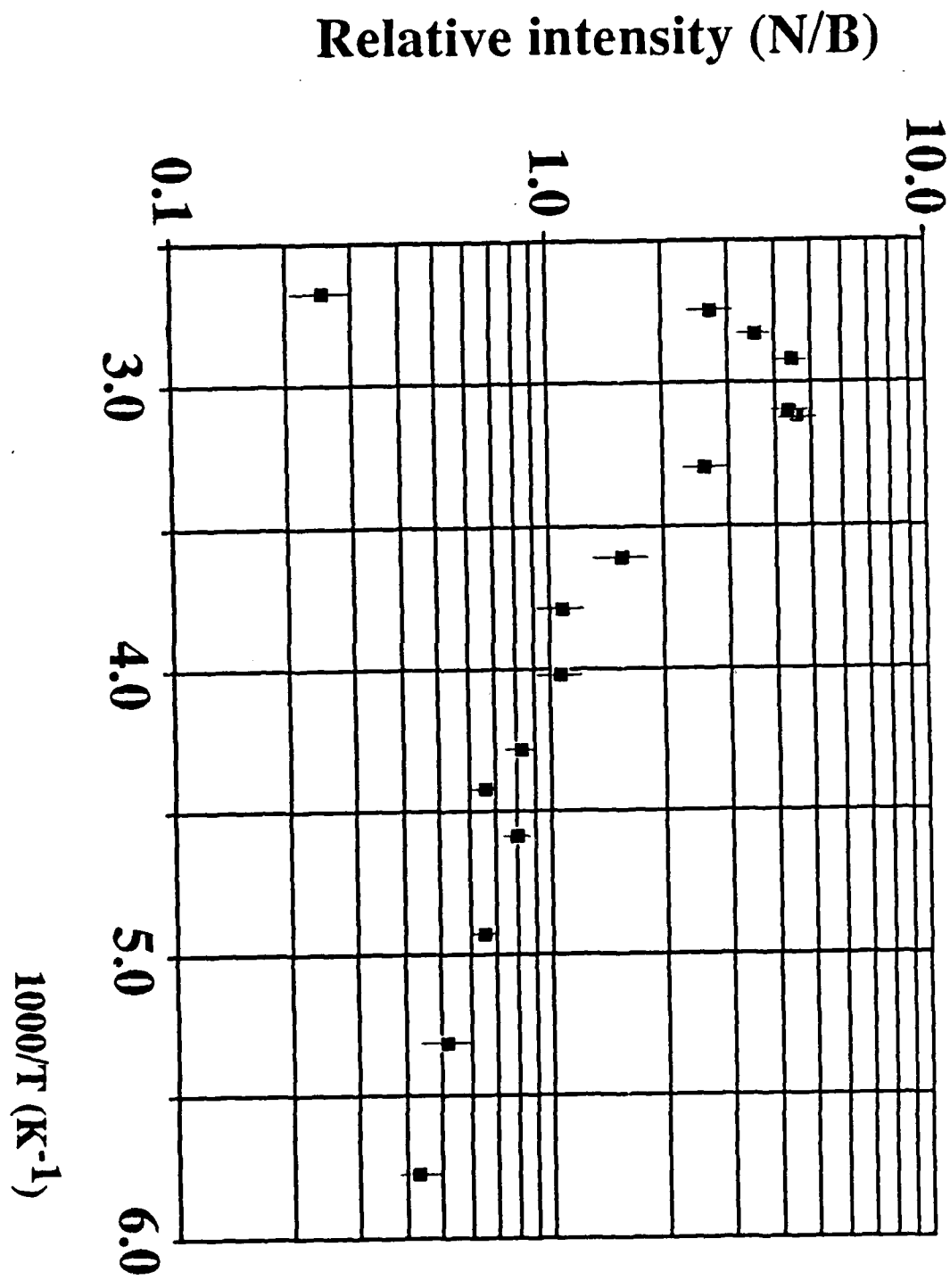
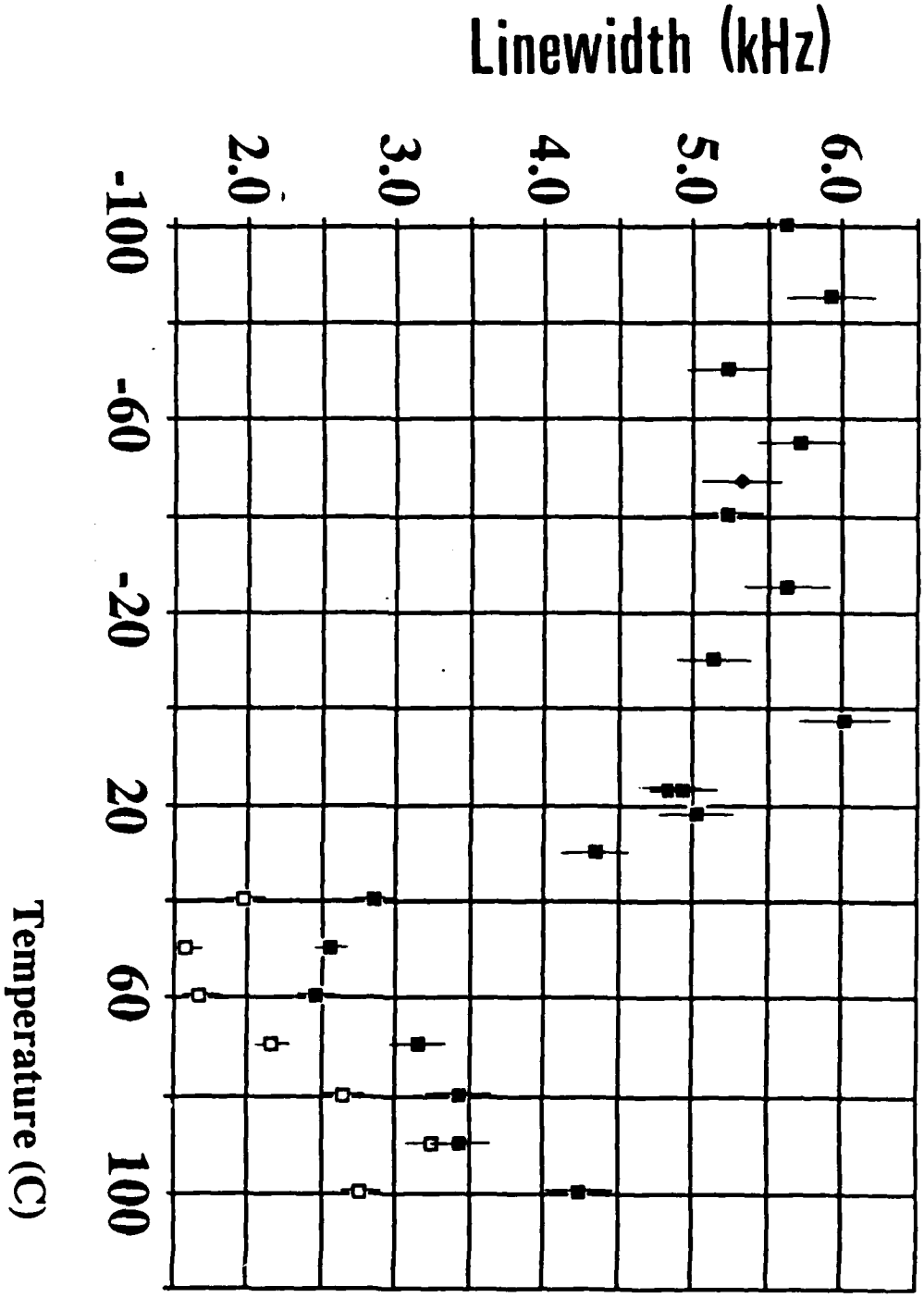


Fig. 3



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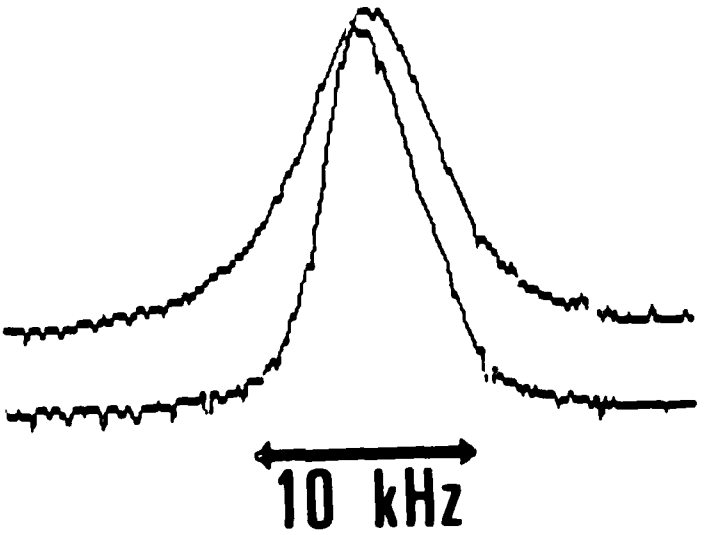
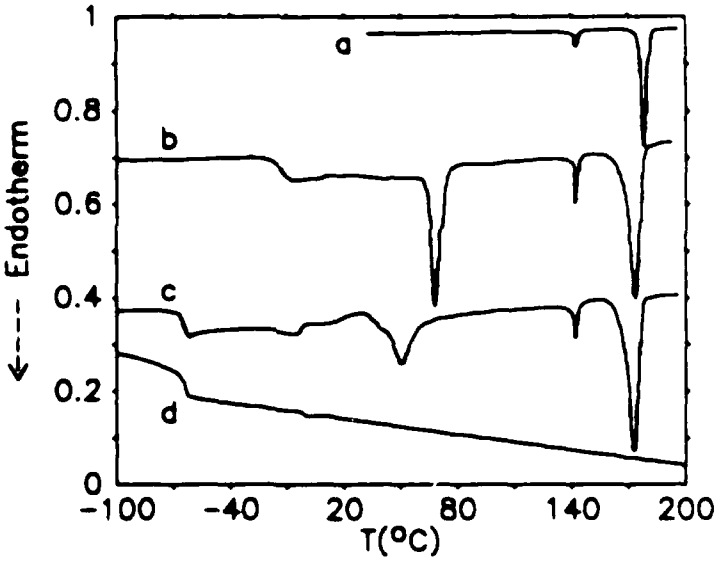


Fig. 5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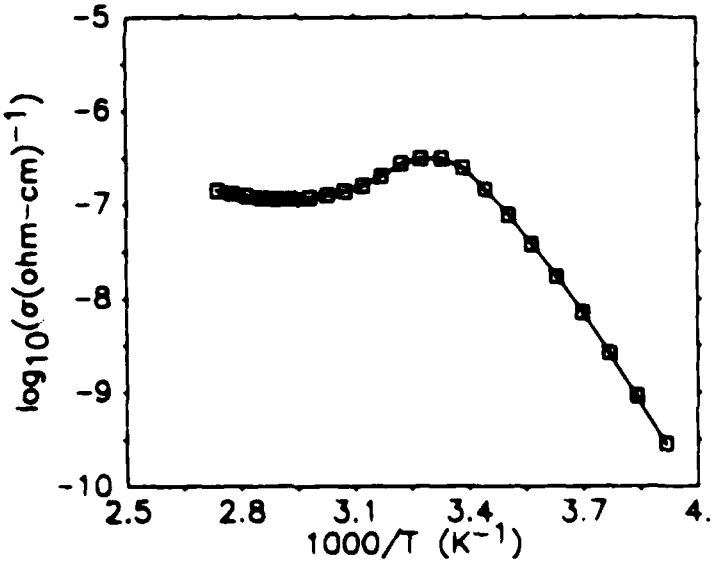

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